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JOHNSON MATTHEY PUBLIC LIMITED COMPANY

2-4 Cockspur Street

Trabalgos Square

LONDON

SW14 5BA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

00536268007

4. Title of the invention

IMPROVEMENTS IN EMISSIONS CONTROL

5. Name of your agent (if you have one)

IAN CARMICHAEL WISHART

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Date 8 June 1999

I. C. WISHART

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IMPROVEMENTS IN EMISSIONS CONTROL

5 The invention concerns improvements in emissions control, especially from internal combustion engines such as diesel and other lean-burn engines.

Lean-burn engines present problems in that it is difficult to reduce NO_x emissions in the presence of oxygen. Compression ignition ("diesel") engines and some types of gasoline
10 engines emit combustible particulate ('soot'). Although engine design, fuelling strategies and devices such as exhaust gas recirculation can decrease engine-out, NO_x levels, it remains difficult to decrease both NO_x and soot to below modern limits, such as are expected to be prescribed in European Stage IV regulations.

15 The difficulty appears to be greater for low exhaust gas temperatures, for example resulting from engine design such as light duty turbo-charged direct injection diesel engines, especially if fitted with EGR, or from light duty generally.

One particularly effective treatment for diesel exhaust is that marketed by
20 Johnson Matthey PLC as the "Continuously Regenerating Trap" ("CRT" -RTM). In the CRT system as disclosed in EP-A-0341832 an oxidation catalyst converts NO in the exhaust to NO₂, the gas enriched with NO₂ is passed into a filter for the soot and the NO₂ causes facile combustion of the soot, thus continuously regenerating the filter and preventing blocking. The CRT is especially suited to so-called heavy-duty diesel engines as used in buses and
25 larger trucks, where exhaust gas temperatures are generally relatively high.

In the case of turbo-charged direct injection engines used in light duty applications such as cars and light trucks, the exhaust gases are relatively cool, which with other factors makes the CRT system rather less effective than with heavy duty engines.

30

The invention provides a process of treating internal combustion engine exhaust gas containing O₂, NO_x, unburnt gaseous hydrocarbon ("HC"), CO and soot, comprising:

- i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO₂;
- ii. treating the product of step i to oxidise NO to NO₂;
- 35 iii. collecting soot; and
- iv. combusting the collected soot by reaction with the NO₂ and possibly any O₂ left

over after step i.

The invention also provides a system for treating such internal combustion engine
5 exhaust gas, comprising:

a first catalyst to receive engine exhaust gas and effective to promote oxidation of
inter alia HC therein;

a second catalyst receiving the product of the first catalyst and effective to promote
oxidation of NO to NO₂;

10 a filter effective to collect soot and retain it until combusted by said NO₂ and
possibly any O₂ left over after the first catalyst.

Since the gas contains soot, the first and second catalysts are suitably supported on a
structure permitting passage of fine solid particles. The structure preferably provides through
15 passages, for example in a honeycomb having at least 50, possibly more, the range 100-900
cells/inch² being generally preferred. The honeycomb may be composed structurally of
ceramic or metal. Such ceramic may be for example alumina, silica, titania, zirconia or
combinations such as example cordierite or silicon carbide. Such metal may be for example a
refractory steel for example Fecralloy. Such metal may make it practicable to provide more
20 passages per square inch, eg up to 1200. Alternative monolithic supports are available, and it
is intended to include static fluid mixers and the like, as required and subject to routine
testing.

The structure carries a coating ('washcoat') of high-surface support material for
25 catalytically active components. For the first catalyst the coating and these components are
chosen so that it is effective to remove substantially all the HC. (It will normally effect
oxidation of CO to CO₂ and, to some extent, of NO to NO₂). We believe, although we do not
wish to be confined to such belief, that removing HC before oxidising NO to NO₂ removes
species inhibiting such NO oxidation. Although part of the NO may be converted to NO₂
30 over the first catalyst, unconverted NO is more effectively converted over the second catalyst.

An effect of the first catalyst can be to increase the temperature at the inlet of the
second catalyst to a level at which the velocity of NO to NO₂ conversion is sufficient to
provide more NO₂: the subsequent soot combustion reactions are also then faster.

The resulting temperature should not of course be in a range at which NO_2 formation is equilibrium B limited.

5 To obtain an adequate reaction rate over the first catalyst, its inlet temperature is preferably maximised by disposing that catalyst as close as possible to the engine outlet. Thus it is typically mounted in the cylinder block region, for example on the exhaust gas manifold before or after a turbo-charger if used. To attain or increase such temperature rise, additional fuel *eg* diesel fuel, may be dosed upstream of the first catalyst and oxidised thereon.
 10 Alternatively or additionally, the engine inlet fuel injection profile may be adjusted to increase the HC, or more conveniently the CO, content of the raw exhaust gas. Preferably such measures to increase gas temperature continue to provide a lean gas composition. Enrichment with HC and/or CO may be continuous or, preferably, intermittent and initiated upon the detection of appropriate exhaust gas conditions. However attained, the temperature
 15 at the outlet of the first catalyst stage is preferably at least 200, and up *eg* to 500 C.

Preferably the first catalyst has a very low light-off temperature for both the CO and HC oxidation reactions. This is an additional benefit during parts of the engine operating cycle in which exhaust gas temperatures are temporarily low, *eg* during idle.

20 Whereas the second catalyst may have the same composition as the first, it may be designed to be more effective for the NO to NO_2 reaction, and the temperature and/or space velocity, for example, may be different as between the two catalysts. Thus the conditions for the HC oxidation and NO oxidation may be independently optimised. The temperature in the
 25 second catalytic step is preferably in the range 150 to 350 C. (Since oxidation of NO is not strongly exothermic, there is little difference between inlet and outlet temperatures).

In the catalysts the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with others *eg* rhodium. The exact
 30 composition of the catalyst is chosen to suit local requirements. Desirably they have relatively high (*eg* 10-150 g/ft³) loadings of platinum, and optionally may have other catalyst components such as rhodium or palladium or catalyst promoter compounds.

The soot filter may be any capable of collecting the soot without causing excessive

back-pressure. Its detailed specification is chosen according to the particular engine characteristics and the regulations to be met. It may be a ceramic wall flow filter, a ceramic foam filter, ceramic fibre filter, sintered metal or wire mesh filter of any suitable type. It may provide for removal of 50 to 100 preferably at least 60, more preferably 85, or greater, of the measured soot in the exhaust gas. There may be a fail-safe bypass or a two-stage filter to cater for a situation where the filter would otherwise be blinded or blocked under certain engine operating conditions. If desired, the filter may be catalysed to assist combustion. A variety of catalysts are known to be suitable, and these include one or more oxides of vanadium, cerium, and mixed Cs/La/V oxide and supported PGMs. The invention includes the possibility of initiating combustion of the soot if required, for example if the engine operating conditions are such that considerable soot is being/has been generated but the gas temperatures are rather too low for significant combustion; for example initiation may be by providing electric heating of a portion of the filter. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and steam.

The invention provides also an engine in combination with a system as herein defined and a process of operating such an engine.

In this combination the first catalyst may be disposed close to the source of exhaust gas, to obtain a maximum convenient operating temperature and reaction rate therein. The outlet gas from that catalyst may undergo cooling, for example in a non-insulated or finned pipe, before entering the second catalyst.

The combination may include expedients such as EGR. The invention may be combined with means to decrease NO_x in the gases leaving the system, which may include lean NO_x catalyst or systems incorporating addition of reductant or ammonia and possibly a NO_x absorber.

The combination may include sensors for at least one of: fuel composition; air/fuel ratio at engine inlet; exhaust gas compositions at critical stages; pressure drop. If engine inlet adjustment and/or fuel injection is used, then a temperature sensor after the first catalyst, and possibly before that catalyst and/or at the inlet of the NO oxidation catalyst are preferably provided. The control system may include also indicator means informing the engine

operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of eg start-up, varying load and chance fluctuations, and to inject fuel into the exhaust gas.

5

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power source. Most usefully it is a light duty engine as defined above, especially powering a passenger car or light truck or van. Generally "light" means less than 3500kg unladen weight. This may typically correspond to a cylinder capacity to 6.0 litres and a power output up to 300 KW. The invention is potentially of value for engine for other duties.

Desirably the engine is fuelled with low sulphur fuel, ie containing less than 50 ppm w/w sulphur, calculated as elemental S, for example "city diesel" or "Swedish MK-1".

The invention is illustrated with reference to the accompanying drawings, in which: figure 1 is a schematic drawing of a system according to the invention; figure 2 is a graph comparing the conversions of NO to NO₂ in the presence of HC (prior art) and absence of HC (invention).

Referring to figure 1, a light-duty turbo-charged direct-injection diesel engine (not shown) discharges its exhaust, containing inter alia HC and soot, into a system comprising reactors 10 and 12, connected together for gas flow at region 14. Region 14 is shown by pecked lines to indicate that the connection may be short or may be relatively long, for example with reactor 10 at the engine outlet and reactor 12 under the vehicle body. Such a long connection may itself provide cooling or may include a finned region. Reactor 10 optionally includes at its inlet 16 the sparging spray injector 18. It essentially includes bed 20, of catalyst primarily for oxidation of HC and CO, the HC content of the gas entering bed 20 being HC exhausted by the engine, possibly augmented by HC injected at 18. Control means (not shown) responsive to the temperature of the gas leaving bed 20 regulates engine inlet conditions and HC injection at 18, to keep the temperature of bed 20 high enough for sufficiently rapid HC oxidation.

Reactor 12 contains at its inlet the bed 22 of catalyst primarily for oxidation of NO to NO₂. The gas leaving bed 22, enriched in NO₂, passes into soot filter 24, where soot is trapped and oxidised by reaction with the NO₂ and O₂. Beds 22 and 24 constitute a "CRT" system. The gas, now substantially soot-free, may pass out to atmosphere if air quality regulations permit. Optionally the system may include, in the same reactor or possibly in a separate one, bed 26, charged with NO_x absorption material, possibly with an injector (not shown) for reductant or ammonia between 24 and 26, and possibly with a catalyst for reduction of NO_x to N₂.

Each bed in the system is in the form of a ceramic honeycomb, with (except filter 24) an alumina washcoat carrying active material.

EXAMPLE 1

A synthetic exhaust gas of the following composition v/v was used:

CO ₂	4.5 %
H ₂ O	4.5 %
O ₂	12.0 %
CO	200 ppm
NO	400 ppm
C ₃ H ₆	0 or 400ppm or 800ppm
N ₂	balance.

This was passed over a 1% w/w platinum on gamma alumina catalyst in particle form in a laboratory reactor at temperatures between 150°C and 500°C. This reactor is known to represent a typical exhaust catalyst consisting of platinum on an alumina washcoat on a honeycomb. The compositions of the outlet gas are shown in figure 2.

The plots for gas containing 400ppm and 800ppm HC (propylene) show there is very little conversion below about 200°C. However, in the absence of hydrocarbon (as removed in bed 20), already there is 20% conversion at 150°C and 85% conversion at 200°C. It is evident that once the HC (represented by C₃H₆) has been removed in the first oxidation step

the oxidation of NO to NO₂ can take place more completely, affording more NO₂ for the combustion of particulate in the subsequent step of CRT. Bearing in mind the cool exhaust gas temperatures met with in modern light duty diesel engine designs, the significantly improved conversion at temperatures below 200°C resulting from the removal of HC, is particularly useful.

EXAMPLE 2

The exhaust of a 4 cylinder turbo-charged direct injection Diesel engine of 2.5 litre capacity with EGR and operated at an air-fuel weight ratio of about 30 was fed to the first of 2 catalytic stages of a system as shown in fig 1 of the drawings. The inlet exhaust gas composition v/v was:

15	CO ₂	5.0%
	H ₂ O	4.9%
	O ₂	13.0%
	CO	800 ppm
	NO	100 ppm
20	N ₂	balance

Catalysts 20 and 22 comprised platinum group metal supported on an alumina-containing washcoat on a 400 cpsi cordierite honeycomb. Catalyst 20 was mounted just outside the engine exhaust manifold after the turbo-charger; catalyst 22 was 1.0m downstream in an underfloor position. For some runs this was adjusted by injection of Diesel fuel using sparger 18, giving a lower but still lean air/fuel ratio. Comparative runs were carried out using at 20 another sample of the same washcoated honeycomb but without catalytic material. Runs were made at a range of load levels, giving temperatures in the range of 225° to 325°C, measured at 22 inlet. The outlet gas was analysed for NO, and total NO_x and NO₂ calculated by difference. The table shows the concentration of NO and NO₂ at representative temperatures.

Temp°C		225°		275°		325°	
N oxide		NO	NO ₂	NO	NO ₂	NO	NO ₂
No Fuel	cat	82	5	78	36	68	63
	non-cat	96	1	80	18	70	54
+ Fuel	cat	71	3	73	33	84	42
	non-cat	65	3	78	26	88	36

- If is evident that, except at the lowest temperature in presence of added fuel, the use of the
- 5 first stage catalyst gives a significantly higher concentration of NO₂, thus providing for more efficient combustion of collected soot on filter 22.

CLAIMS

1. A process of treating internal combustion engine exhaust gas containing O₂, NO_x unburnt gaseous hydrocarbon ("HC"), CO and soot, comprising:
 - 5 i. oxidising a substantial part of the HC, with possibly some oxidation of NO to NO₂;
 - ii. treating the product of step i to oxidise NO to NO₂;
 - iii. collecting soot; and
 - iv. combusting the collected soot by reaction with the NO₂ and possibly any O₂ left over after step i.
- 10 2. Process according to claim 1 in which at least steps i and ii are effected catalytically.
3. Process according to claim 1 or claim 2 carried out over:
 - 15 i a first catalyst adapted to be fed with engine exhaust gas and effective to promote oxidation of HC therein;
 - ii a second catalyst adapted to be fed with the product of i and effective to promote oxidation of NO to NO₂;
 - iii a filter effective to collect soot and to retain it until combusted by said NO₂ and any O₂ left over after catalyst i.
- 20 4. Process according to claim 3 in which the catalysts are honeycomb-supported.
5. Process according to claim 4 in which the cell density of the honeycomb is in the range 100-900 per square inch.
- 25 6. Process according to any one of the preceding claims in which the conditions of reaction in steps/catalysts i and ii are independently optimised.
7. Process according to any one of the preceding claims in which catalyst i is disposed
30 close to the source of exhaust gas, whereby to obtain a maximum convenient operating temperature and reaction rate.
8. Process according to claim 6 or claim 7 in which the gas leaving step/catalyst i undergoes cooling and then enters step/catalyst ii.

9. Process according to any one of the preceding claims including injection of combustible upstream of the step catalyst i, whereby to increase the temperature at which that step operates.
- 5
10. Process according to claim 9 in which said combustible is provided by modifying engine settings to pass more HC and/or generate more CO.
11. Process according to any one of the preceding claims in which the first catalyst has a very low light-off temperature for HC and CO oxidation.
- 10
12. Process according to any one of the preceding claims in which the temperatures °C are in the ranges
- i 200°-500°
- 15 ii 150°-350°.
13. Process according to any one of the preceding claims including also NOx-removal downstream of soot combustion.
- 20 14. Process according to any one of claims 1 to 14 including also a regenerable NOx absorber downstream of the collecting trap.
15. Process according to claim 14 including catalytic NOx-removal downstream of the NOx absorber.
- 25
16. System for carrying out a process according to any one of the preceding claims comprising:
- i. a first catalyst to receive engine exhaust and effective to promote oxidation of HC therein;
- 30 ii. a second catalyst receiving the product of the first catalyst and effective to promote oxidation of NO to NO₂;
- iii a filter effective to collect soot and to retain it until combusted by said NO₂ and any O₂ left over after the first catalyst.

17. System according to claim 16 in which the catalysts are honeycomb-supported.
18. System according to claim 17 in which the cell density of the honeycomb is in the
5 range 100-800 per square inch.
19. A diesel engine having a system according to any one of claims 16 to 18 connected to its exhaust.
- 10 20. An engine according to claim 19 which is one designed for light duty applications.
21. An engine according to claim 19 or 20 which is of the turbo-charged direct injection type.
- 15 22. An engine according to any one of claims 19 to 21 fed with a fuel containing less than 50 ppm w/w as S of sulphur compounds.
25. A process, system or engine, substantially as described and as illustrated by the foregoing specific description.

5

IMPROVEMENTS IN EMISSIONS CONTROL

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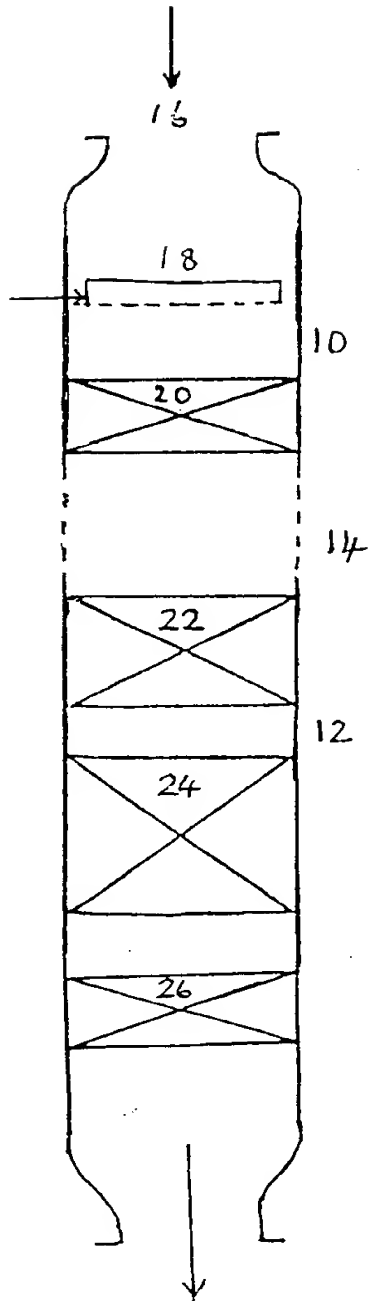
Abstract

15 An improved system for treating the aftertreatment of exhaust gases, especially from light duty engines in cars and light trucks, comprises a first catalyst (20) effective to oxidise hydrocarbons, a second catalyst (22) effective to convert NO to NO₂, a trap (24) for particulates, on which particulates may combust with the NO₂, and optionally a NO_x absorption material (26).

20

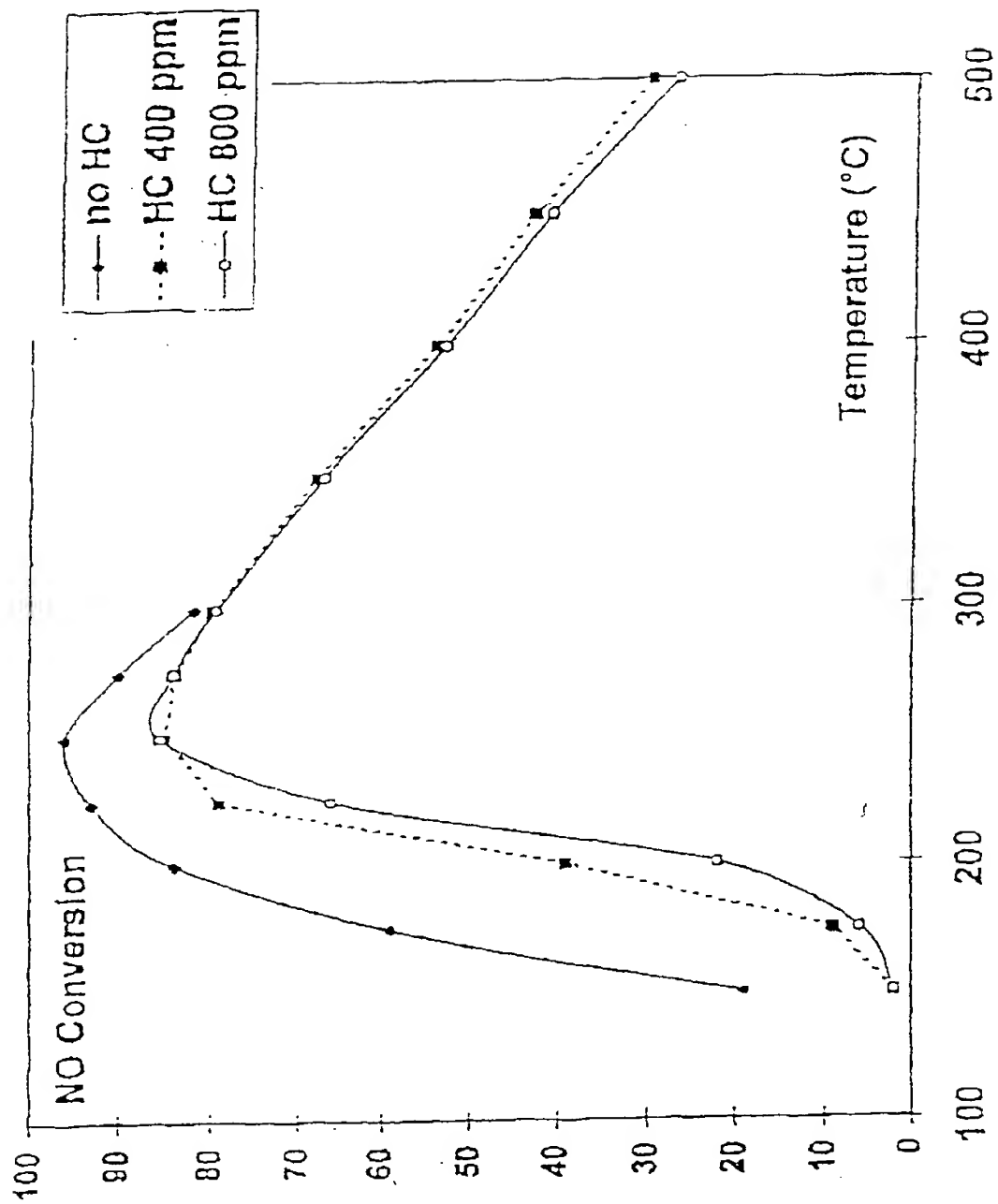
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Fig 1



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Fig. 2



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Johnson Matthey

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